1. 40 points.

(a) Fill in the appropriate symbol: =, >, or <:

i. $\Delta S_T > 0$

ii. $\Delta G < 0$ for a spontaneous process at constant $T$ and $P$

iii. $S_T > 0$

iv. $\mu_A = \mu_B$ when A and B are in equilibrium

v. $S(T = 0 K) = 0$

(b) Draw the periodic boundary conditions in the grid below, and calculate the total interaction energy (in terms of $D$) for the boxed spin.

\[
\begin{array}{cccccc}
- & + & - & - & - & + \\
+ & + & + & + & + & + \\
+ & + & - & - & + & + \\
- & - & + & - & - & - \\
- & - & - & - & - & + \\
+ & + & + & + & + & + \\
\end{array}
\Rightarrow
\begin{array}{cccc}
-2 & -2 & 0 & -4D \\
-2 & 6 & -4 & -4 \\
0 & 0 & 2 & 0 \\
0 & 4 & 2 & 2 \\
\end{array}
\]

(c) Find the heat needed to raise the temperature of 2.50 mol graphite from 298 K to 323 K, if $C_{Pm} = 8.23 \text{ J K}^{-1} \text{ mol}^{-1}$. Solution:

\[
q = nC_{Pm}\Delta T = (2.50 \text{ mol})(8.23 \text{ J K}^{-1} \text{ mol}^{-1})(323 \text{ K} - 298 \text{ K}) = 514 \text{ J}.
\]

(d) The $\Delta_{vap}H^\circ$ of water at 373 K is 40.65 kJ mol$^{-1}$. Find $\Delta_{vap}S^\circ$. Solution:

\[
\Delta_{vap}S^\circ = \frac{\Delta_{vap}H^\circ}{T_b} = \frac{(40.65 \text{ kJ mol}^{-1})(10^3 \text{ J} / \text{kJ})}{373 \text{ K}} = 109 \text{ J K}^{-1} \text{ mol}^{-1}.
\]

2. An imaginary engine operates on a cycle with the $PV$ and $TS$ graphs shown below. (This is not a Carnot cycle.) Calculate the efficiency of the engine.

Solution: The efficiency is the net work done divided by the heat input, which in this case is

\[
\epsilon = \frac{-w_1 + w_2 + w_3 + w_4}{q_1 + q_4}.
\]
We include both $q_1$ and $q_4$ because the heat is being added to the system during these steps, and we don’t count the heat that’s released in steps 2 and 3 because that heat is just released into the surroundings. The net work can be calculated from the area of the parallelogram described by the cycle in the $PV$ graph, which is $(2.0 \text{ bar})(2.0 \text{ L}) = 4.0 \text{ bar L} = 400 \text{ J}$. The heat input can be estimated (more approximately) by the area under a line from roughly $(S,T) = (80,95)$ to $(130,430)$ in the $TS$ graph, which is the sum of the areas of a rectangle and a triangle:

$$q_1 + q_4 \approx [(95)(130 - 80) + \frac{1}{2}(430 - 95)(130 - 80)] \text{ J} = 13125 \text{ J}.$$ 

So we get an efficiency of

$$\epsilon = \frac{400 \text{ J}}{13125 \text{ J}} = 0.030.$$ 

Why is this engine so inefficient? It’s partly because the straight lines in the $PV$ curve deviate substantially from the curve for the reversible isothermal and adiabatic expansions, so the work is not being maximized, and also because the low temperature is a significant fraction of the high temperature.

3. Calculate the absolute molar entropy of CO at 498 K, assuming that only translations and rotations contribute. The rotational constant is 1.93 cm$^{-1}$. **Solution**: We use the Sackur-Tetrode equation for the translational contribution, and Eq. 9.43 for the rotational contribution:

$$S_{m,\text{trans}} = R \left\{ \frac{5}{2} + \ln \left( \frac{(2\pi mk_BT)^{3/2}RT}{N_A\mathcal{P}} \right) \right\}$$

$$\left( \frac{2\pi mk_BT}{h^2} \right)^{3/2} = \left( \frac{2\pi (28.0 \text{ amu})(1.661 \cdot 10^{-27} \text{ kg amu}^{-1})(1.381 \cdot 10^{-23} \text{ J K}^{-1})(498 \text{ K})}{(6.626 \cdot 10^{-34} \text{ J s})^2} \right)^{3/2} = 3.097 \cdot 10^{32} \text{ m}^3$$

$$\frac{RT}{N_A\mathcal{P}} = \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(498 \text{ K})}{(6.022 \cdot 10^{23} \text{ mol}^{-1})(1.00 \cdot 10^5 \text{ Pa})} = 6.876 \cdot 10^{-26} \text{ m}^3$$

$$S_{m,\text{trans}} = R \left\{ \frac{5}{2} + \ln \left( (3.097 \cdot 10^{32})(6.876 \cdot 10^{-26} \text{ m}^{-3}) \right) \right\} = 19.374 R$$

$$S_{m,\text{rot}} = R \left( \ln \left( \frac{k_BT}{B} + 1 \right) \right) = R \left( \ln \left( \frac{0.6950 \text{ cm}^{-1} \text{ K}^{-1}}{1.93 \text{ cm}^{-1}} \right)(498 \text{ K}) + 1 \right) = 6.189 R$$

$$S_m = S_{m,\text{trans}} + S_{m,\text{rot}} = 19.374 R + 6.189 R = 25.563 \text{ J K}^{-1} \text{ mol}^{-1}.$$ 

4. The vapor pressure of acetone is 0.0526 bar at 263.8 K and 0.526 bar at 312.7 K. Find the latent enthalpy of vaporization. **Solution**: The pressures and temperatures are related by the Clausius-Clapeyron equation. If we go back to how that equation was derived, recall that it connects any two sets of $P$ and $T$. We chose to integrate from the reference pressure at 1.00 bar and the normal boiling point $T_b$, but we could also have integrated from any $P_1, T_1$ and gotten essentially the same equation:

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta_{\text{vap}}H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\Delta_{\text{vap}}H = R \ln \left( \frac{P_2}{P_1} \right) \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]^{-1}$$

$$= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{0.526}{0.0526} \right) \left[ \frac{1}{263.8 \text{ K}} - \frac{1}{312.7 \text{ K}} \right]^{-1}$$

$$= 32295 \text{ J mol}^{-1} = 32.3 \text{ kJ mol}^{-1}.$$